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Per MÅRTENSSON	Group Art Unit: 3724
Application No.: 10/073,239	Examiner: Unassigned
Filed: February 13, 2002	
For: α-ALUMINA COATED CUTTING TOOL	

CLAIM FOR CONVENTION PRIORITY

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

The benefit of the filing date of the following prior foreign application in the following foreign country is hereby requested, and the right of priority provided in 35 U.S.C. § 119 is hereby claimed:

Swedish Patent Application No. 0100520-6

Filed: February 16, 2001

In support of this claim, enclosed is a certified copy of said prior foreign application. Said prior foreign application was referred to in the oath or declaration. Acknowledgment of receipt of the certified copy is requested.

Respectfully submitted,

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Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.

(71)	*Sökande* *Applicant (s)*	*Sandvik AB, Sandviken SE*
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För Patent- och registreringsverket
For the Patent- and Registration Office

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Avgift
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α-ALUMINA COATED CUTTING TOOL

The present invention describes a cutting tool for metal machining, having a substrate of cemented carbide, cermet or ceramics and on the surface of said substrate, a hard and wear resistant coating is deposited. The coating is adherently bonded to the substrate and covering all functional parts of the tool. The coating is composed of one or more refractory layers of which at least one layer consists of strongly textured alfa-alumina (α-Al_2O_3).

It is well known that for cemented carbide cutting tools used in metal machining, the wear resistance of the tool edge considerably can be increased by applying thin, hard surface layers of metal oxides, carbides or nitrides with the metal either selected from the transition metals from the groups IV, V and VI of the Periodic Table or from the group silicon, boron and aluminium. The coating thickness usually varies between 1 and 15 μm and the most widespread method for depositing such coatings is CVD (Chemical Vapor Deposition).

The practice of applying a pure ceramic layer such as alumina on top of layers of metal carbides and nitrides for further improvements of the performance of a cutting tool was early recognized as is evidenced in U.S. Pat. Reissue No. 29,420 (Lindström et al) and U.S. Pat. No. 3,836,392 (Lux et al). Alumina coated cutting tools are further disclosed in U.S. Pat. Nos. 4,180,400 (Smith et al), 4,619,866 (Smith et al), 5,071,696 (Chatfield et al), 5,674,564 (Ljungberg et al) and 5,137,774 (Ruppi) wherein the Al_2O_3 layers comprise the α- and κ-phases and/or combinations thereof. E.g. in U.S. 4,180,400, an alumina deposition process is disclosed where tetravalent ions of e.g. Ti, Zr or Hf are added in their halide compositions to the reaction gas mixture in order to deposit essentially single phase κ-Al_2O_3.

The practice of mixing different metal halides in order to deposit composite ceramic coatings is evidenced in U.S. Pat. Nos. 4,701,384 (Sarin et al), 4,745,010 (Sarin et al) and 5,827,570 (Russell) where processes for depositing mixtures of e.g. Al_2O_3 and ZrO_2 are described.

In further efforts to improve the cutting performance of alumina coated cemented carbide cutting tools, particularly in the machining of nodular cast iron, deposition processes yielding

fine-grained, single phase α-Al_2O_3 exhibiting specific crystal orientation (texture) and surface finish are disclosed in U.S. Pat. Nos. 5,654,035 (Ljungberg et al), 5,766,782 (Ljungberg), 5,834,061 (Ljungberg) and 5,980,988 (Ljungberg).

None the less the machining of nodular cast iron is still considered to be a demanding metal working operation. This is particularly obvious in heavy and interrupted machining operations where an α-Al_2O_3 coated tool often suffers from extensive flaking of the alumina layer from the tool substrate. Hence, it is the object of the present invention to provide onto a hard tool substrate a relatively thick Al_2O_3-layer of the polymorph alpha with a desired microstructure and crystallographic texture by applying a deposition process with suitable nucleation and growth conditions such that the acquired properties of the Al_2O_3-layer provide an alumina coated cutting tool with improved cutting performance in steel, stainless steel, cast iron and, in particular, in nodular cast iron.

According to the present invention there is provided a cutting tool for metal machining such as turning (threading and parting), milling and drilling comprising a body of a hard alloy of sintered cemented carbide, cermet or ceramic onto which a hard and wear resistant refractory coating is deposited. Said coating comprising a structure of one or several refractory layers of which at least one layer consists of alumina with a layer thickness of 0.5-25 μm, preferably 1-10 μm. The alumina layer consists of essentially single phase α-alumina with a pronounced columnar grain-structure.

Figures 1 and 2 show Scanning Electron Microscope (SEM) cross-section micrographs at 8000X magnification of an α-alumina layer according to the present invention (Figure 1) and an Al_2O_3-layer according to prior art technique (Figure 2). Figure 1 displays the characteristic columnar microstructure and Figure 2 displays a more coarse-grained and equiaxed microstructure typical of prior art.

Figures 3 and 4 show X-ray diffraction patterns for α-Al_2O_3 layers deposited according to the invention (Figure 3) and according to prior art technique (Figure 4).

Figures 5 and 6 show Light Optical Microscope (LOM) micrographs of worn cutting edges of a coated cutting insert according

to present the invention, Figure 5, and according to prior art, Figure 6.

As a consequence of the fine-grained structure perpendicular to the growth direction of the α-alumina layer according to the invention, the cutting edges of the tool obtain a smooth surface finish, which compared to prior art α-Al_2O_3 coated tools, results in an improved surface finish also of the workpiece being machined.

The invented α-Al_2O_3 layer may also contain a small amount of residues of a "texture modifying agent" which may be present in the form of separate grains or in the form of a solid solution with the alumina grains. The concentration of said residues can be found in the range 0.01-10, preferably 0.01-5 and most preferably less than 1 percent by weight of the α-alumina coating and the amount of said residues is low enough not to affect the intrinsic properties of the alumina coating itself.

The α-Al_2O_3 layer according to the present invention exhibits a preferred crystal growth orientation in the [300]-direction which is determined by X-ray Diffraction (XRD) measurements. Figures 3 and 4 show X-ray diffraction patterns for α-Al_2O_3 layers deposited according to the invention (Figure 3) and according to prior art technique (Figure 4). The very pronounced growth orientation in the [300]-direction is easily perceived from Figure 3.

A Texture Coefficient, TC, can be defined as:

$$TC(hkl) = \frac{I(hkl)}{I_0(hkl)}\left\{\frac{1}{n}\sum\frac{I(hkl)}{I_0(hkl)}\right\}^{-1}$$

where

I(hkl) = measured intensity of the (hkl) reflection.

I_O(hkl) = standard intensity of the ASTM standard powder pattern diffraction data card number 43-1484.

n = number of reflections used in the calculation, (hkl)reflections used are: (012), (104), (110), (113), (024), (116), (300).

According to the present invention, TC for the set of (300)-crystalplanes is larger than 1.5, preferably larger than 3 and most preferably larger than 5.

The applied coating on the cutting tool may in addition to the strongly textured α-Al_2O_3 layer(s) contain at least one layer comprising a carbide, nitride, carbonitride, oxycarbide and/or

oxycarbonitride of the metal elements (Me_1, Me_2, ...) selected from the groups IVB, VB and VIB of the Periodic Table or from the group B, Al and Si and/or mixtures thereof, $(Me_1, Me_2, ...)C_xN_yO_z$, $TiC_xN_yO_z$ being preferred. In a preferred embodiment the α-Al_2O_3 layer according to the present invention is preferably the outermost layer of the coating and the $TiC_xN_yO_z$ layer is the innermost layer of the coating. But metal-$C_xN_yO_z$ layers may also be deposited on top of the alfa-alumina layer(s).In a preferred embodiment the outer layer on top of the outermost α-Al_2O_3 layer is TiN.

The textured α-Al_2O_3 layer according to the invention is deposited by a CVD (Chemical Vapor Deposition) or a PACVD (Plasma Chemical Vapor Deposition) technique where the tool substrates to be coated are held at a temperature 950-1050 °C and are brought in contact with a hydrogen carrier gas containing one or more halides of aluminium, and a hydrolysing and/or an oxidizing agent. The oxidation potential of the CVD reactor atmosphere prior to the nucleation of Al_2O_3 is kept at a low level with a concentration of water vapor (H_2O) or other oxidizing species such as CO_2, O_2, etc., below 5 ppm. The nucleation of α-Al_2O_3 is started up by sequencing of the reactant gases that HCl and CO_2 are entering the reactor first in an Ar and/or H_2 atmosphere followed by $AlCl_3$. When nucleation of α-Al_2O_3 has occurred, a sulphur catalyst, preferably H_2S, is added to the reaction gas mixture in order to obtain the enhanced deposition rate.

Surprisingly it has been found that when adding small amounts of other metal halides, such as $ZrCl_4$ or $HfCl_4$, to the reaction gas mixture during the growth period of the α-Al_2O_3 layer, a crystallographic structure is attained having a very strong texture in the [300]-direction. The concentration of a second halide, a so-called texture modifying agent, preferably $ZrCl_4$, shall be in the range of 0.05-10, preferably 0.2-5 and most preferably 0.5-2 percent by volume of the total reaction gas volume.

The invented CVD method described above has made it possible to deposit α-Al_2O_3 layers with a desired micro structure and orientation and, said layers can be grown to a relatively large thickness, and surprisingly, still retain its excellent adhesion properties to the tool substrate as well as adding the desired improvement in wear resistance of the cutting tool which will demonstrated in a forthcoming example. In order to further improve the

properties of the coated cutting tool the surface may also be smoothened by a standard brushing technique.

The exact conditions of the CVD process depend to a certain extent upon the design of the equipment being used. It is within the purview of the person skilled in the art to determine whether the requisite texture and coating morphology have been obtained and to modify nucleation and the deposition conditions in accordance with the present specification, if desired, to affect the degree of texture and coating morphology.

EXAMPLE 1

A) Cemented carbide cutting inserts with the composition 6.0 weight-% Co, and balance WC were coated with a 3 µm thick layer of TiCN in a standard CVD process. In subsequent process steps during the same coating cycle, a 7 µm thick layer of α-Al_2O_3 was deposited by the method described below.

A reaction gas mixture comprising H_2, HCl and CO_2 was first introduced into the CVD-reactor. The reaction gases were sequentially added in the given order. After a pre-set time $AlCl_3$ was allowed into the reactor. During the deposition of Al_2O_3, H_2S was used as a catalyst and $ZrCl_4$ as texture modifying agent. The gas mixtures and other process conditions during the Al_2O_3 deposition steps comprised:

	Step 1.	Step 2.
CO_2	5%	5%
$AlCl_3$	2%	2%
$ZrCl_4$	-	1%
H_2S	-	0.3%
HCl	2%	6%
H_2	Balance	Balance
Pressure	55 mbar	55 mbar
Temperature	1010°C	1010°C
Duration	1 hour	3 hours

XRD-analysis showed a texture coefficient, TC(300), of 6.2 (average of ten inserts) of the single α-phase of the Al_2O_3-layer. SEM-micrographs showed a 7 µm thick Al_2O_3-layer with a pronounced columnar grain-structure as is demonstrated in Figure 1.

B) Cemented carbide substrate of A) was coated with TiCN (3 µm) and Al_2O_3 (7 µm) as set forth in A) except that the Al_2O_3 deposition process was carried out according to prior art technique.

The gas mixtures and other process conditions during the Al_2O_3 deposition steps comprised:

	Step 1.	Step 2.
CO_2	5%	5%
$AlCl_3$	2%	2%
$ZrCl_4$	-	-
H_2S	-	0.3%
HCl	2%	6%
H_2	Balance	Balance
Pressure	55 mbar	55 mbar
Temperature	1010°C	1010°C
Duration	1 hour	3 hours

XRD-analysis showed a texture coefficient, TC(300), of 0.9 (average of ten inserts) of the single α-phase of the Al_2O_3-layer. The XRD-pattern is displayed in Figure 4. SEM-micrographs showed a 7 µm thick Al_2O_3-coating with an equiaxed grain-structure as depicted in Figure 2.

EXAMPLE 2

Coated tool inserts from A), and B) were brushed using a standard production method in order to smoothen the coating surface. The cutting inserts were then tested with respect to edge line and rake face flaking in a turning operation, facing in nodular cast iron (AISI 60-40-18, DIN GGG40), a machining test which has proven to be a good benchmark test on the strength of the coating adhesion.

Cutting data:
Speed = 250 m/min,
Depth of cut = 2.0 mm
Feed = 0.2 mm/rev.
Coolant was used.

The results are expressed in the table below as percentage of the edge line in cut on which flaking of the coating has occurred, and furthermore, the rake face area subjected to flaking in relation to the total contact area between the rake face and the workpiece chip. The numbers shown in the table below are average values for 5 tested cutting edges.

Coating	Edge line flaking	Rake face flaking
According to A	4%	<1%
According to B	53%	62%

Figures 5 and 6 show Light Optical Microscope (LOM) micrographs of worn cutting edges tested according to the above described method. Figure 5 shows the wear pattern of a coated cutting insert according to present the invention and Figure 6 shows the wear pattern of coated cutting insert according to prior art technique.

CLAIMS

1. Cutting tool comprising a body of sintered cemented carbide, cermet or ceramic and on which at least on the functional parts of the surface of the body, a hard and wear resistant coating is applied and said coating comprising a structure of one or more refractory layers of which at least one layer consists of alumina characterised in that said alumina layer having a thickness of 0.5-25 µm, preferably 1-10 µm, and consisting of essentially single phase α-alumina textured in the [300]-direction with a texture coefficient larger than 1.5, preferably larger than 3, and most preferably larger than 5, the texture coefficient being defined as:

$$TC(hkl) = \frac{I(hkl)}{I_0(hkl)}\left\{\frac{1}{n}\sum\frac{I(hkl)}{I_0(hkl)}\right\}^{-1}$$

where
$I(hkl)$ = measured intensity of the (hkl) reflection
$I_o(hkl)$ = standard intensity of the ASTM standard powder pattern diffraction data, card number 43-1484.
n = number of reflections used in the calculation
(hkl) reflections used are: (012), (104), (110), (113), (024), (116) and (300).

2. Cutting tool according to claim 1 characterised in that said α-alumina layer contains between 0.01-10, preferably 0.01-5 and most preferably less than 1 percent by weight of residues of a texture modifying agent.

3. Cutting tool according to any of the preceding claims characterised in having at least one layer of thickness 0.1-10 µm, preferably 0.5-5 µm, comprising a nitride, carbide, carbonitride, oxycarbide and/or oxycarbonitride of the metal titanium ($TiC_xN_yO_z$) and that said layer is in contact with the α-alumina layer.

4. Cutting tool according to claim 3 characterised in that the outer layer is α-alumina.

5. Cutting tool according to any of the preceding claims characterised in that the outer layer is TiN.

6. Cutting tool according to any of the preceding claims characterised in that the surface of the coated cutting tool is smoothened by means of a brushing operation.

7. A method for producing a coated cutting tool, wherein at least one refractory layer consisting of α-alumina textured in the

[300]-direction as per claim 1, is deposited by CVD (Chemical Vapor Deposition) or PACVD (Plasma CVD) by which the tool surface to be coated is brought in contact with a hydrogen carrier gas containing one or more halides of aluminium and a hydrolysing and/or an oxidizing agent characterised in that the oxidation potential of the CVD-reactor atmosphere prior to the nucleation of α-alumina is kept at a low level with a concentration of water vapor (H_2O) or other oxidizing species preferably below 5 ppm, and that the nucleation of α-alumina is started up by the sequencing of the reactant gases that HCl and CO_2 are entering the reactor first in an H_2 and/or Ar atmosphere followed by $AlCl_3$, that the temperature is held at 950-1050°C during the nucleation period, that during the growth period of the α-Al_2O_3 layer a sulphur catalyst and a texture modifying agent are added, the catalyst preferably being H_2S and the texture modifying agent preferably being $ZrCl_4$ or $HfCl_4$ or mixtures thereof.

8. A method according to claim 7 characterised in that the addition of a texture modifying agent, preferably $ZrCl_4$ to the reaction gas mixture shall be in the range of 0.05-10, preferably 0.2-5 and most preferably 0.5-2 percent by volume of the total reaction gas mixture.

SUMMARY

The present invention describes a coated cutting tool for metal machining. The coating is composed of one or more layers of refractory compounds of which at least one layer consists of essentially single-phase α-alumina with a pronounced columnar grain-structure and strong texture in the [300]-direction. The alumina layer is deposited by CVD (Chemical Vapor Deposition) and the preferred microstructure and texture are achieved by adding a second metal halide, a texture modifying agent, to the reaction gas. When coated cemented carbide cutting tools according to the invention are used in the machining of steel or cast iron, several important improvements compared to prior art have been observed, particularly in the machining of nodular cast iron.

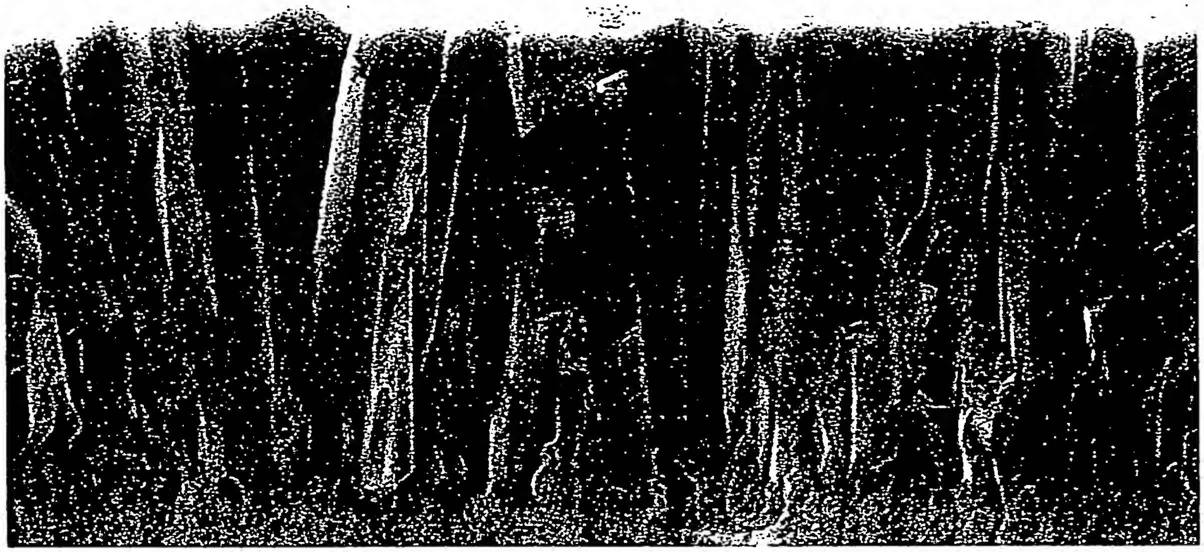

Figure 1

Figure 2

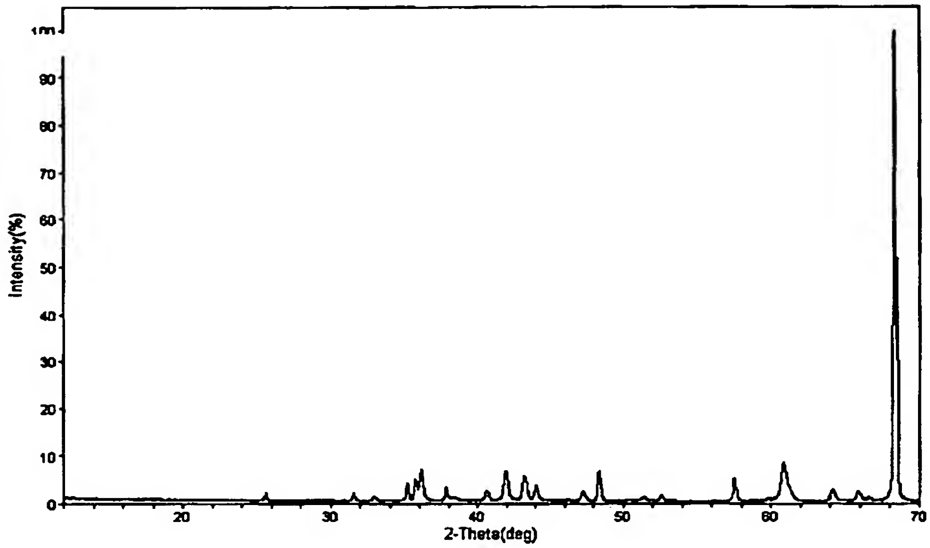

Figure 3

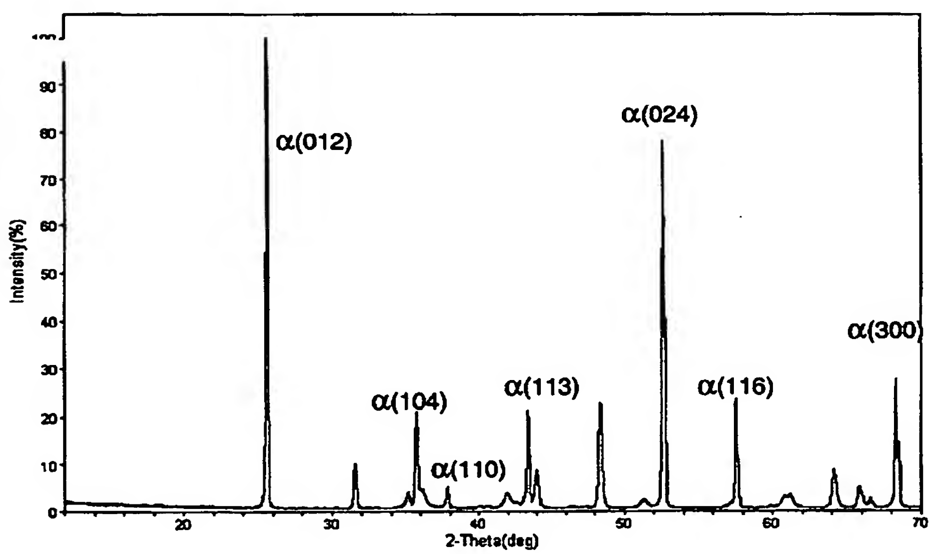

Figure 4

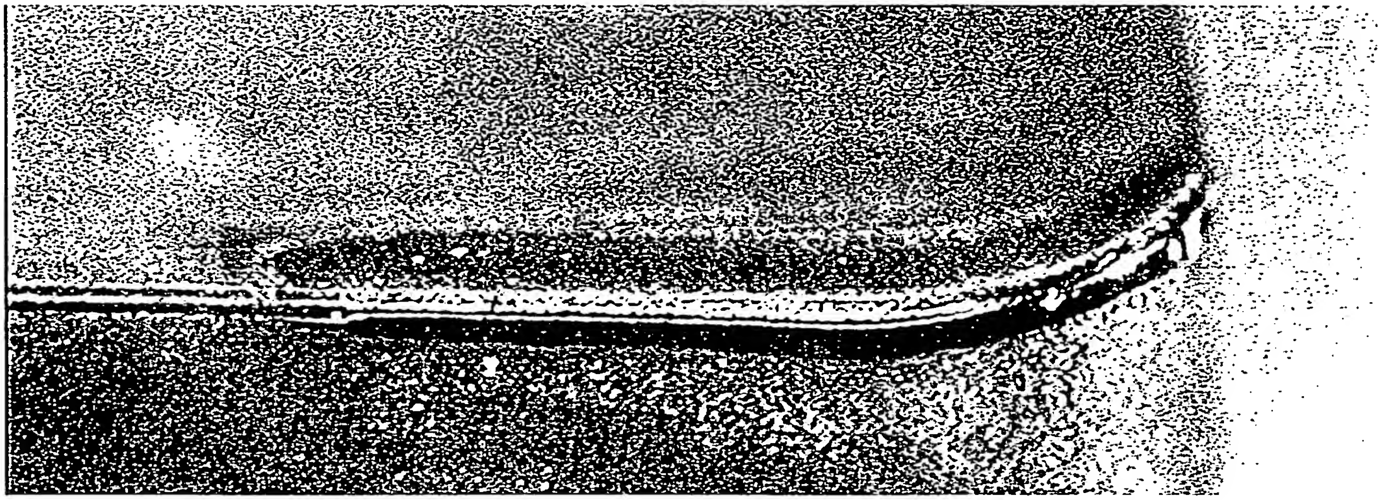

Figure 5

Figure 6